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VARIABILITY IN REQUIRED OZONE DOSES FOR REMOVING PHARMACEUTICALS FROM WASTEWATER EFFLUENTS

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EXTENDED ABSTRACT

Aim of study. The aim of the present study was to investigate the ozone dosage required to remove active pharmaceutical ingredients (APIs) from biologically treated wastewater of varying quality originating from different wastewater treatment processes.
Methods. Secondary effluents from six Swedish wastewater treatment plants (WWTP) were spiked with 42 APIs (nominal concentration 1μg/L) and treated with different O_3 doses (0.5-12.0 mg/L ozone) in bench-scale experiments[1]. Concentrations of APIs were measured by SPE extraction using OASIS HLB cartridges followed by quantification using LC-MS-MS[2].
Results. For each wastewater effluent a profile of sensitivity of each API to a range of ozone doses were generated.
In order to obtain a parameter to compare the sensitivity of APIs to ozone in each wastewater the specific dose of ozone required to achieve one decade of removal of each investigated API (DDO_3) was determined for each effluent by fitting a first order equation to the remaining concentration of API at each applied ozone dose. Equation 1 describes the remaining API concentration in relation to its initial concentration after a specific O_3 dose is delivered (DO_3). The equation contains the O_3 dose required to remove 90% of the API as a constant (here noted as decadic dose of O_3 DDO_3. The fitted parameter is named the decadic dose of O_3, DDO_3.

$$(Eq.1) \qquad \log\left(\frac{C}{C_o}\right)=\frac{-DO_3}{DDO_3} \Leftrightarrow C=C_o\cdot 10^{-\left(\frac{DO_3}{DDO_3}\right)}$$

Ozone dose requirements for APIs were found to vary significantly between wastewater effluents depending on their matrix characteristics.
The specific ozone dose was normalized to the dissolved organic carbon (DOC) of each effluent as shown in Table 1. The DDO_3/DOC ratios were comparable for each API between the effluents. 15 of the 42 investigated APIs could be classified as easily degradable (DDO_3/DOC≤0.7), while 19 were moderately degradable (0.7<DDO_3/DOC≤1.4) and 8 were recalcitrant towards O_3-treatment (DDO_3/DOC >1.4).
With this estimates of the required ozone dose required to remove any of the investigated APIs may be attained by multiplying the experimental average DDO_3/DOC obtained with the actual DOC of any effluent. The method predicts results which agrees with removal rates and ozone doses found in literature.

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Technical University of Denmark

Variability in required ozone doses for removing pharmaceuticals from wastewater effluents

Henrik R. Andersen

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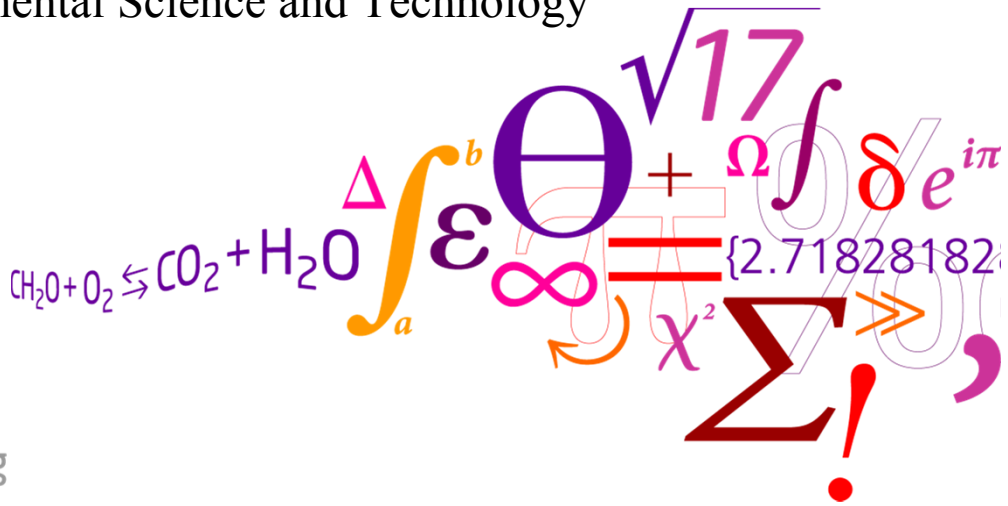

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Objectives

- **The overall objective of this study is to find a method to estimate the required ozone dose for removal of a micropolutants - exemplified by active pharmaceutical ingredients (APIs) – in WWTP effluents of different quality.**

- **The specific objective of this study was to identify the required O_3 doses to achieve 90% degradation of selected different types of APIs.**

Work done

- **The removal of 42 APIs by different added ozone doses were investigated in effluents from 6 Swedish WWTP.**

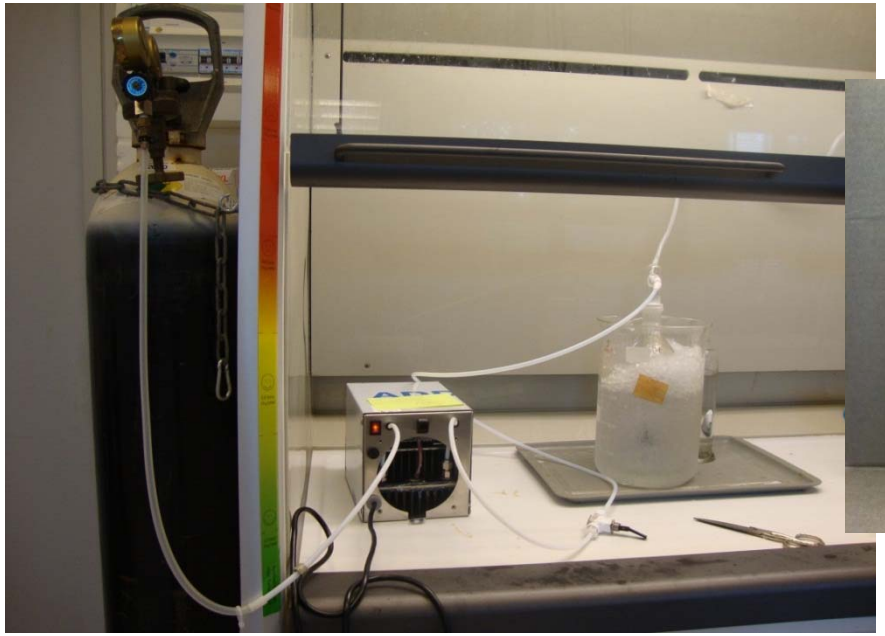
- **A curve was fitted to the O_3 dose- API removal data in order to estimate the required O_3 doses to achieve 90% degradation of each pharmaceutical in each effluent.**

- **It was attempted to correlate the effective O_3 doses in different effluents with basic wastewater parameters (i.e., DOC, COD, alkalinity)**
  - **Rather than using the second order rate constants.**
  - **$k_{O3,API}$ >10^4 $M^{-1}s^{-1}$, easily degraded.**
  - **$k_{O3,API}$ < 10^4 $M^{-1}s^{-1}$, are more recalcitrant to O_3**
  - **You cannot determine the O_3 doses needed (matrix effects)**

(Hollender et al., 2009; Huber et al., 2003; Zimmermann et al., 2011).

Experiment and analysis

- 6 Effluents (secondary treatment) from WWTP (different treatment processes , matrix characteristic-COD, N-NH_4^+, alkalinity) were spiked with an APIs mixture (45) of nominal concentration of 1 µg/L and treated by varying ozone doses in triplicate.
- Preparation of O_3 stock solution (~35mg/L O_3)
- Delivered O_3 dose (0,5 <O_3<12 mg/L) was measured with the indigo method (λ=600nm) in Milli-Q water.
- Bottles were placed in a waterbath at T=15°C
- Quantification of APIs - Liquid chromatography-tandem mass-spectrometry (LC-MS/MS)



A single parameter which describes the removal results by different ozone doses

- Our parameter, DDO_3, is the O_3 dose required to achieve 90% removal of a micropolutant in an effluent.
- The concept was based on the equation suggested by James Bolton that correlates EED (electrical energy dose) of energy intensive treatment processes with the concentration reduction of the treatment target:

$$\log\left(\frac{C}{C_i}\right) = \frac{-1}{E_{EO}} EED$$

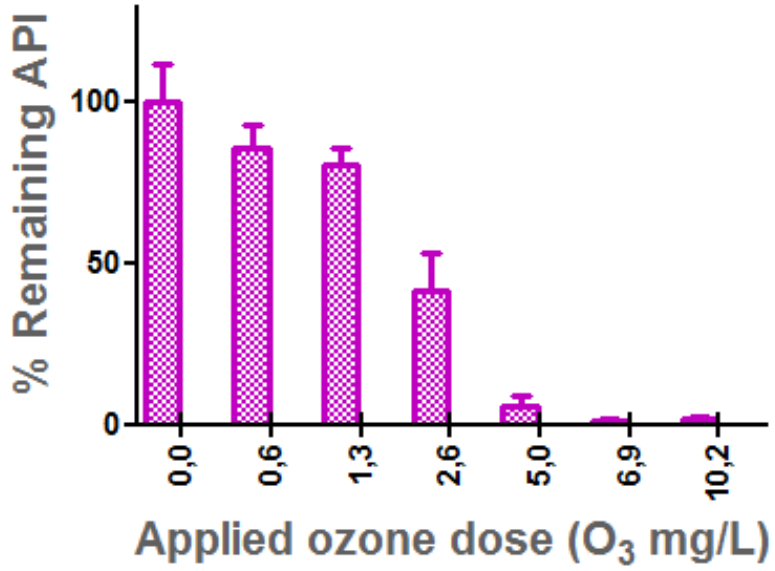
where C_i and C is the initial and the final concentration, respectively, EED is the electrical energy dose in kWh/m³ and E_{EO} is the electrical energy per order.

- This approach has been used before for the O_3 of estrogenic compounds from WW (Hansen et al., 2010):

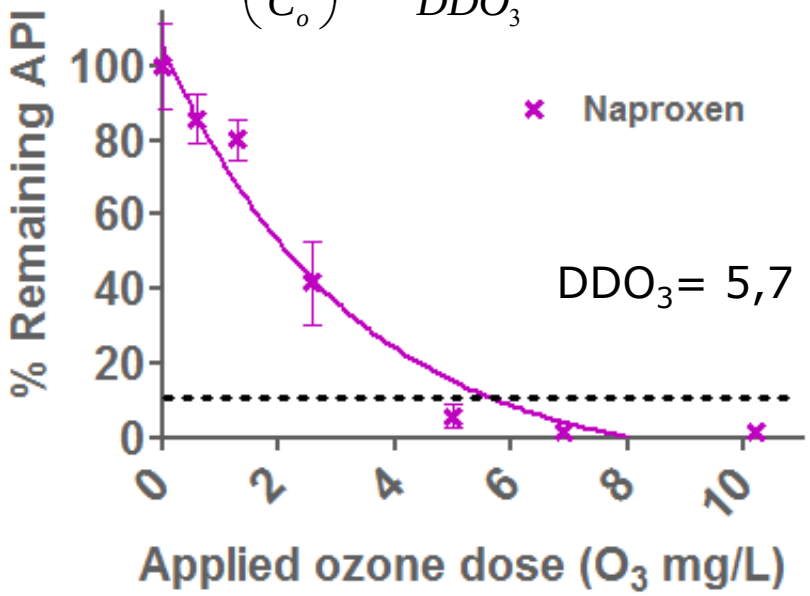
$$\log\left(\frac{C}{C_o}\right) = -\frac{DO_3}{DDO_3} \Leftrightarrow C = C_o \cdot 10^{-\left(\frac{DO_3}{DDO_3}\right)}$$

Bolton, J.R., et al., Pure and Applied Chemistry (2001) 73(4), 627-637.
Hansen, K.M.S. *et al.*, *Water Science and Technology* **2010,** *62*, 649-657

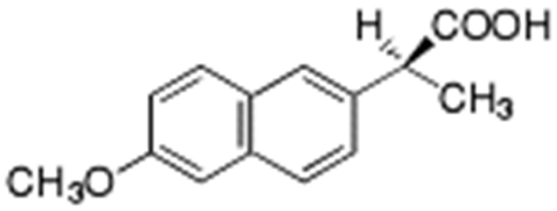
Example of curve fitting to determine DDO_3



$$\log\left(\frac{C}{C_o}\right) = -\frac{DO_3}{DDO_3} \Leftrightarrow C = C_o \cdot 10^{-\left(\frac{DO_3}{DDO_3}\right)}$$



DDO_3= 5,7 mg/L



$k_{O3,API}$= 2,62·10⁴ - 2,97·10⁵ (M^1s^{-1})
$k_{HO\bullet,API}$= 8,4 ·10⁹ (M^1s^{-1})

Benitez et al. *Chemosphere*, **2009**, 77, 53-59.

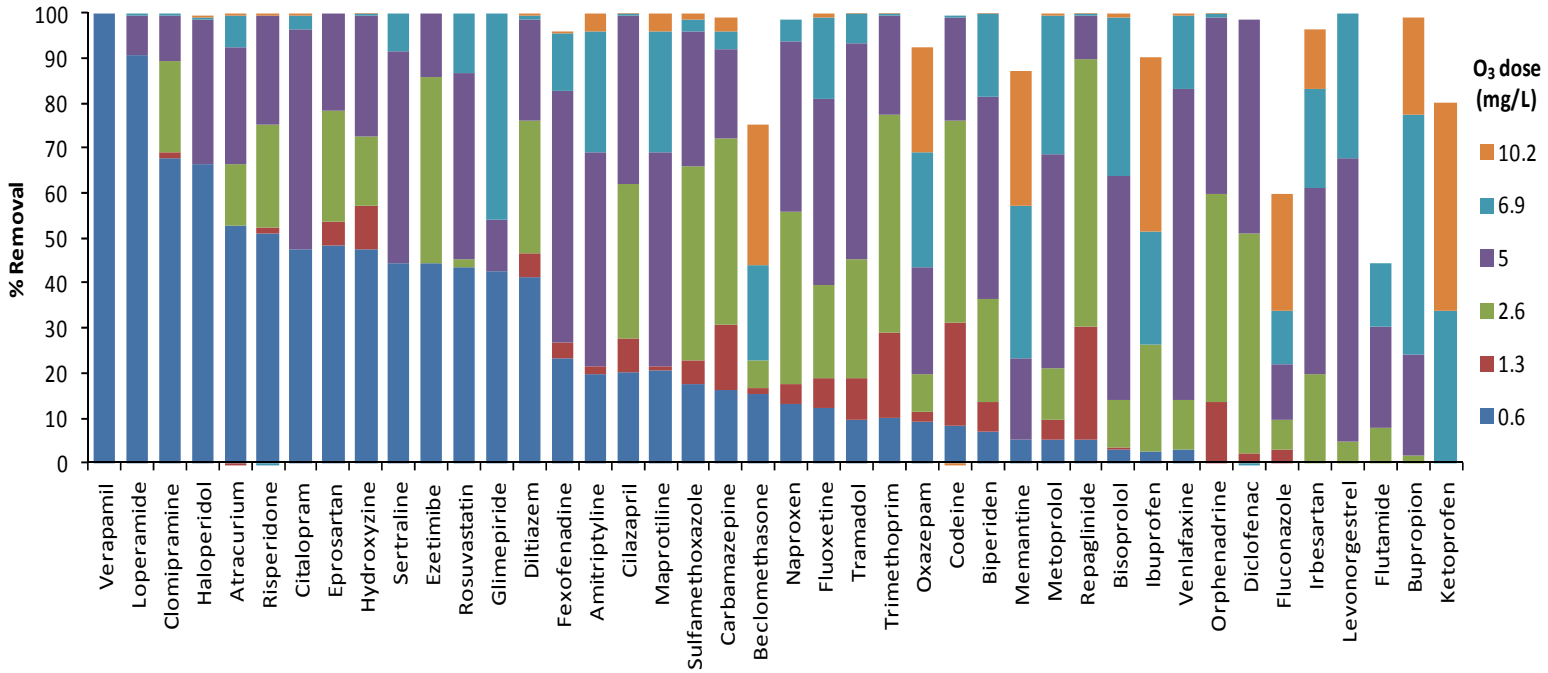
Naproxen: a non-steroidal anti-inflammatory drug

Results: WW effluents characteristics

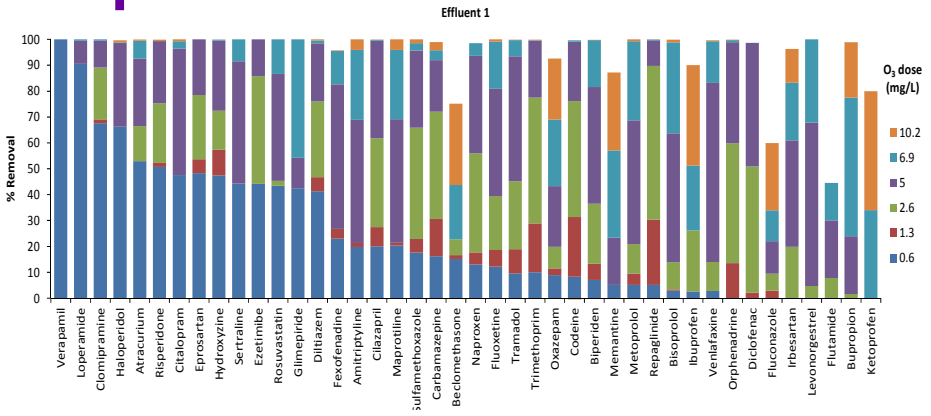
Table 1. Source and characterization of the wastewater effluents.

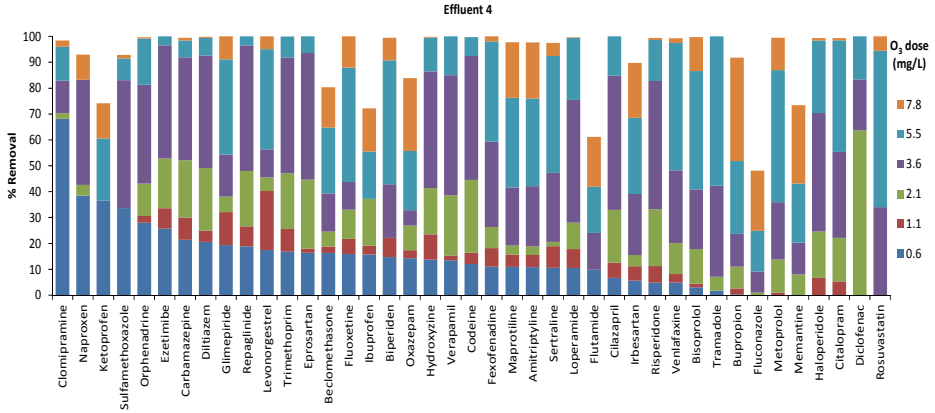
WWTP	Källby 1	Källby 2	Björnstorp	Öresundsverket	Sjölunda	Nykvarnsverket
	Eff1	Eff2	Eff3	Eff4	Eff5	Eff6
COD, mg/L	29	51	30	36	90	44
DOC, mg/L	7.5	6.5	5.2	8.1	13.7	8.4
Alkalinity, mg HCO_3^-/L	244	154	185	229	256	164
pH	6.6	6.7	7.0	7.2	6.7	6.8
N-NH_4^+, mg/L	1.36	2.98	0.77	4.93	1.86	5.98
SUVA, (L/mg)/m	2.74	2.94	2.07	2.10	1.86	2.01
A254, cm^{-1}	0.206	0.190	0.107	0.171	0.256	0.168

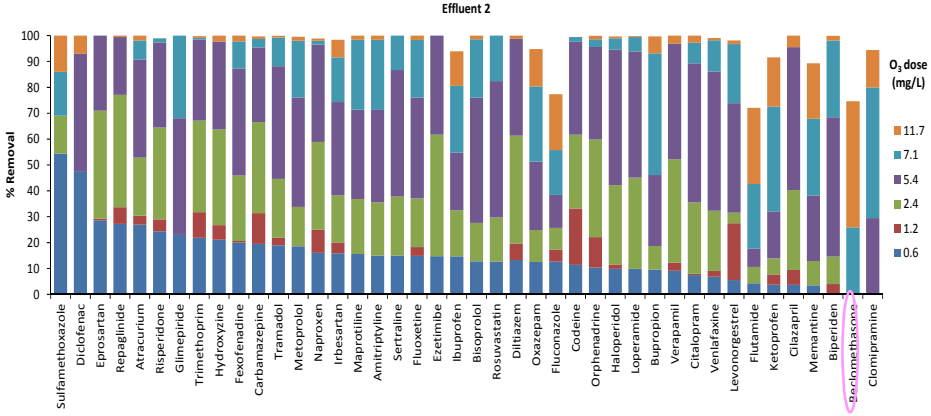
Results: Required O_3 dose to degrade 45 pharmaceuticals in one effluent

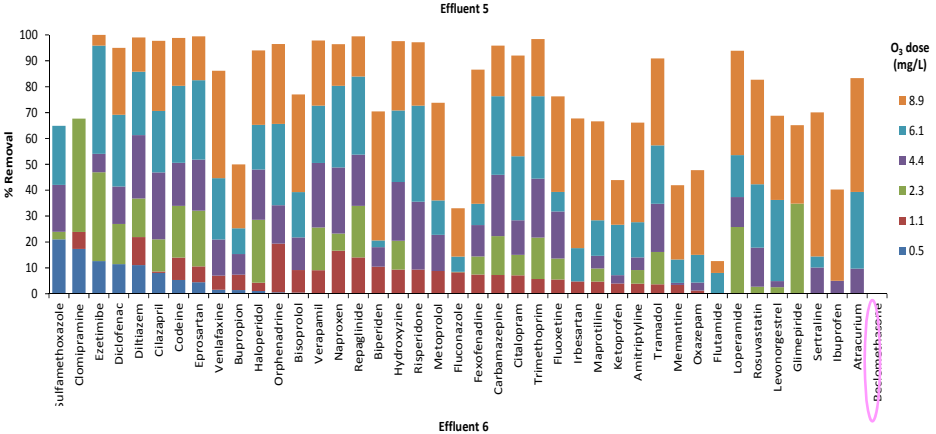


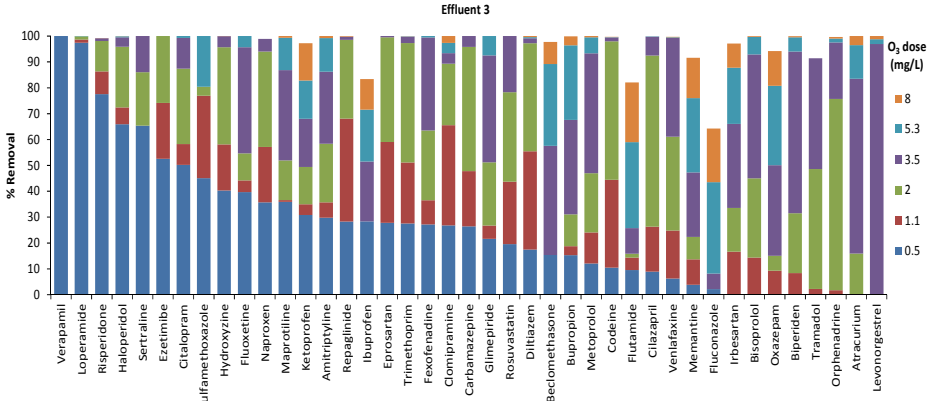
Results: Required O_3 dose to degrade 45 pharmaceuticals in effluents from 6 sources

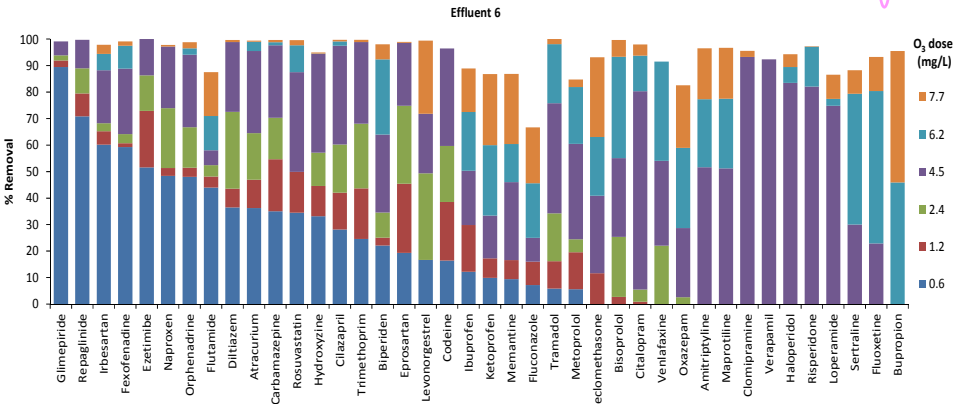




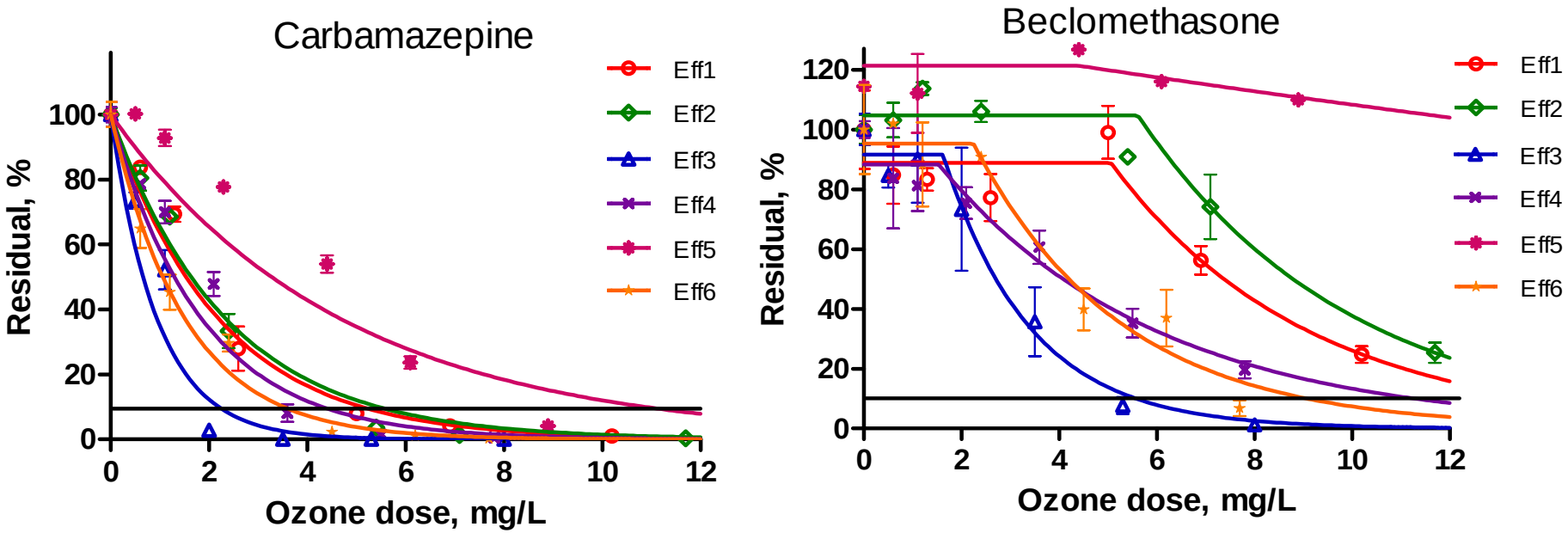






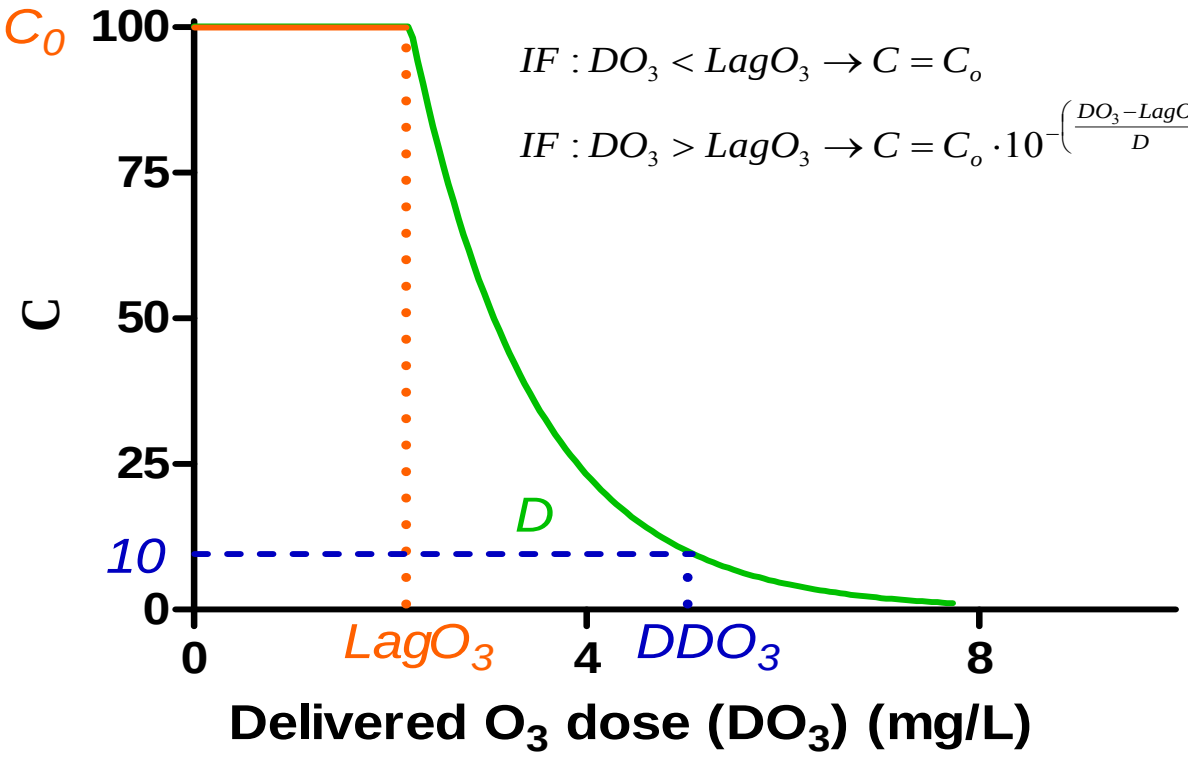


Results: Concentration profiles



- The intersect of the black horizontal line with the 10 % remaining API concentration (*y*-axis) indicates the corresponding DDO_3. T-bar represent standard deviation with n=3.

Suggested enhanced ozone results treatment



$$IF: DO_3 < LagO_3 \rightarrow C = C_o$$

$$IF: DO_3 > LagO_3 \rightarrow C = C_o \cdot 10^{-\left(\frac{DO_3 - LagO_3}{D}\right)}; \qquad DDO_3 = D + LagO_3$$

API	DDO_3 (ppm O_3) Eff1	Eff2	Eff3	Eff4	Eff5	Eff6	[DDO_3/DOC] Eff1	Eff2	Eff3	Eff4	Eff5	Eff6	**Ave**
Easily degradable													
Repaglinide	2.6	3.7	1.8	4.1	8.7	1.5	0.35	0.57	0.35	0.50	0.64	0.18	**0.43**
Ezetimibe	3.2	4.6	1.5	3.8	8.0	2.0	0.43	0.71	0.29	0.47	0.58	0.24	**0.45**
Diltiazem	3.6	3.7	2.2	4.3	8.0	3.9	0.48	0.57	0.42	0.53	0.58	0.47	**0.51**
Eprosartan	3.2	4.9	1.9	4.5	9.1	4.2	0.43	0.76	0.37	0.55	0.66	0.50	**0.55**
Trimethoprim	4.0	4.3	2.1	4.4	9.7	3.9	0.53	0.67	0.40	0.54	0.71	0.47	**0.55**
Clomipramine	2.3	7.3	2.4	3.7	7.5	4.2	0.31	1.13	0.46	0.45	0.55	0.50	**0.57**
Risperidone	3.5	4.7	0.9	5.5	12.1	5.0	0.47	0.73	0.17	0.68	0.88	0.60	**0.59**
Hydroxyzine	3.4	5.7	1.9	4.8	10	4.8	0.45	0.88	0.37	0.59	0.73	0.57	**0.60**
Codeine	4.2	4.9	2.4	4.6	9.2	5.4	0.56	0.76	0.46	0.57	0.67	0.65	**0.61**
Carbamazepine	5.1	5.4	2.2	4.3	10.8	3.5	0.68	0.84	0.42	0.53	0.79	0.42	**0.61**
Naproxen	5.7	5.0	2.5	6.4	10	3.7	0.76	0.77	0.48	0.79	0.73	0.44	**0.66**
Fexofenadine	5.2	5.8	3.0	6.5	9.1	2.9	0.69	0.90	0.58	0.80	0.66	0.35	**0.66**
Orphenadrine	4.5	5.0	3.4	4.8	12.1	4.0	0.60	0.77	0.65	0.59	0.88	0.48	**0.66**
Diclofenac	4.7	5.8	NA*	3.5	10	NA*	0.63	0.90	NA*	0.43	0.73	NA*	**0.67**
Cilazapril	4.5	7.1	2.7	5.7	11	4.0	0.60	1.10	0.52	0.70	0.80	0.48	**0.70**
Moderately degradable													
Loperamide	2.0	4.5	<0.5	5.7	13.3	8.7	0.27	0.70	NA**	0.70	0.97	1.04	**0.74**
Glimepiride	7.0	7.6	3.6	6.7	>>8.9	0.6	0.93	1.18	0.69	0.82	NA**	0.07	**0.74**
Rosuvastatin	5.4	5.6	3.3	5	14.5	4.8	0.72	0.87	0.63	0.61	1.06	0.57	**0.74**
Haloperidole	4.8	7.8	1.5	6.3	11.8	5.9	0.64	1.21	0.29	0.77	0.86	0.71	**0.75**
Sulfamethoxazole	4.8	4.5	3.6	4.5	17.6	NA*	0.64	0.70	0.69	0.55	1.28	NA*	**0.77**
Verapamil	NA*	5.4	<0.5	5.0	10.5	7.5	NA*	0.84	NA**	0.61	0.77	0.90	**0.78**
Tramadole	5.7	5.8	3.4	6.3	13	6.4	0.76	0.90	0.65	0.77	0.95	0.77	**0.80**
Citalopram	5.0	7.8	2.0	7.1	15	5.0	0.67	1.21	0.38	0.87	1.09	0.60	**0.80**
Sertraline	6.4	5.2	1.7	7.9	12	11.6	0.85	0.81	0.33	0.97	0.88	1.39	**0.87**
Venlafaxine	5.3	6.3	3.4	6.4	16.6	9.3	0.71	0.98	0.65	0.79	1.21	1.11	**0.91**
Maprotiline	7.3	6.9	4.1	8.3	13.6	7.2	0.97	1.07	0.79	1.02	0.99	0.86	**0.95**
Bisoprolol	7.2	6.0	3.3	7.3	21	7.2	0.96	0.93	0.63	0.90	1.53	0.86	**0.97**
Amitriptyline	7.3	9.4	3.6	8.3	13.6	7.3	0.97	1.46	0.69	1.02	0.99	0.87	**1.00**
Metoprolol	6.9	6.9	3.8	7.4	18.2	8.8	0.92	1.07	0.73	0.91	1.33	1.05	**1.00**
Biperiden	5.9	6.3	4.3	7.3	23	7.4	0.78	0.98	0.83	0.90	1.68	0.88	**1.01**
Levonorgestrel	6.7	7.3	6.6	6.0	18.2	6.5	0.89	1.13	1.27	0.74	1.33	0.78	**1.02**
Fluoxetine	6.6	6.8	3.1	7.7	20	11.3	0.88	1.05	0.60	0.95	1.46	1.35	**1.05**
Irbesartan	8.7	7.7	5.4	11.5	13.7	4.3	1.16	1.19	1.04	1.41	1.00	0.51	**1.05**
Bupropion	8.1	8.0	5.2	9.3	>>8.9	12.1	1.08	1.24	1.00	1.14	NA**	1.45	**1.18**
Recalcitrant towards ozone degradation													
Oxazepam	12.3	11.3	7.1	13.5	18.4	9.7	1.64	1.75	1.37	1.66	1.34	1.16	**1.49**
Ketoprofen	13.4	12.7	5.5	13.2	23.9	9.7	1.78	1.97	1.06	1.62	1.74	1.16	**1.56**
Memantine	11.4	12.8	7.8	14.5	21.3	10.2	1.52	1.98	1.50	1.78	1.55	1.22	**1.59**
Ibuprofen	11.5	10.9	7.3	14.7	27	10.4	1.53	1.69	1.40	1.81	1.97	1.24	**1.61**
Beclomethasone	20	18	5.8	12	>>8.9	9.2	2.66	2.79	1.12	1.47	NA**	1.10	**1.83**
Atracurium	3.7	6.2	4.4	11	11.1	3.9	0.49	3.13	0.85	1.35	0.81	0.47	**1.18**
Flutamide	>>10.2	25	11.7	17.9	>>8.9	9.4	NA**	3.87	2.25	2.20	NA**	1.12	**2.36**
Fluconazole	15.1	18	10.7	20	>>8.9	22	2.01	2.79	2.06	2.46	NA**	2.63	**2.39**

Ozone dose for removal of the first decade of selected pharmaceuticals in each wastewater

	DDO_3 (ppm O_3)						DDO_3/DOC						
Pharmaceutical	Eff1	Eff2	Eff3	Eff4	Eff5	Eff6	Eff1	Eff2	Eff3	Eff4	Eff5	Eff6	**Ave**
Easily degradable													
Carbamazepine	5.1	5.4	2.2	4.3	10.8	3.5	0.68	0.84	0.42	0.53	0.79	0.42	**0.61**
Naproxen	5.7	5.0	2.5	6.4	10	3.7	0.76	0.77	0.48	0.79	0.73	0.44	**0.66**
Diclofenac	4.7	5.8	NA	3.5	10	NA	0.63	0.90	NA	0.43	0.73	NA	**0.67**
Moderately degradable													
Citalopram	5.0	7.8	2.0	7.1	15	5.0	0.67	1.21	0.38	0.87	1.09	0.60	**0.80**
Metoprolol	6.9	6.9	3.8	7.4	18.2	8.8	0.92	1.07	0.73	0.91	1.33	1.05	**1.00**
Fluoxetine	6.6	6.8	3.1	7.7	20	11.3	0.88	1.05	0.60	0.95	1.46	1.35	**1.05**
Recalcitrant towards ozone degradation													
Memantine	11.4	12.8	7.8	14.5	21.3	10.2	1.52	1.98	1.50	1.78	1.55	1.22	**1.59**
Ibuprofen	11.5	10.9	7.3	14.7	27	10.4	1.53	1.69	1.40	1.81	1.97	1.24	**1.61**
Beclomethasone	20	18	5.8	12	>>8.9	9.2	2.66	2.79	1.12	1.47	NA	1.10	**1.83**

Required ozone doses for removing pharmaceuticals from wastewater effluents.

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